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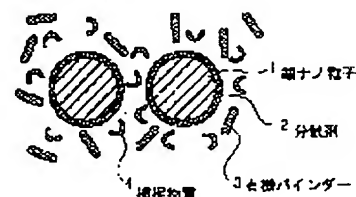
(54) MULTILAYERED WIRING BOARD AND ITS FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To further make finer the circuit pattern of a multilayered wiring board, the vertical continuity hole sections (via holes) of a substrate, etc.

SOLUTION: The circuit pattern is formed by sintering nano-silver paste prepared by stably dispersing fine metallic particles which have a mean particle diameter of 1-100 nm, are composed of gold, silver, copper, etc., and are coated with a dispersant 2 (amine, alcohol, thiol, etc.), capable of coordinating with the metal element contained in the fine metallic particles in an organic solvent at a temperature of $\leq 250^{\circ}\text{C}$. In addition, conductive sections are formed on the inner peripheral surfaces of the via holes by filling up the via holes with the nano-silver paste and sintering the paste at a temperature of $\leq 250^{\circ}\text{C}$. Before printing (a), nano-sized silver particles 1 are stably dispersed (not aggregated) in the organic solvent by the coating action of the dispersant 2. At heating time (b), a trapping material 4 (an acid anhydride, etc.), entraps the dispersant 2. In the state (c), in addition, low-temperature sintered nano-sized silver particles are brought into contact with each other and connected to each other by the shrinking force of a resin.

(a) 印刷前(加熱前)



(b) 加熱時



(c) 樹脂収縮および低温度焼結状態



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Three Dimensional Printing: Rapid Tooling and Prototypes Directly from a CAD Model

Three Dimensional Printing is a process for the manufacture of tooling and functional prototype parts directly from computer models. Three Dimensional Printing functions by the deposition of powdered material in layers and the selective binding of the powder by "ink-jet" printing of a binder material. Following the sequential application of layers, the unbound powder is removed, resulting in a complex three-dimensional part. The process may be applied to the production of metal, ceramic, and metal-ceramic composite parts.

An experiment employing continuous-jet ink-jet printing technology has produced a three-dimensional ceramic part constructed of 50 layers, each 0.005 in. thick. The powder is alumina and the binder is colloidal silica. The minimum feature size is 0.017 in., and features intended to be 0.5000 in. apart average 0.4997 in. apart in the green state and 0.5012 in. apart in the cured state, with standard deviations of 0.0005 in. and 0.0018 in., respectively. Future research will be directed toward the direct fabrication of cores and shells for metal casting, and toward the fabrication of porous ceramic preforms for metal-ceramic composite parts.

1 Introduction

1.1 Motivation. Two needs which are key to industrial productivity and competitiveness are the reduction in time to market for new products and the flexible manufacture of products in small quantities. This work targets a critical subset of the problems that must be overcome in order to achieve shorter product development cycles and flexible manufacturing for mechanical parts. The problems addressed are rapid prototyping, rapid fabrication of tooling, and the low cost manufacture of tooling.

A major contributor to the time to market for new products is the time required to fabricate prototypes. Rapid prototyping can shorten the product development cycle and improve the design process by providing rapid and effective feedback to the designer. Some applications require rapid prototyping of nonfunctional parts for use in assessing the aesthetic aspect of a design or the fit and assembly of a design. Other applications require functional parts. Often, it is advantageous if the functional part is fabricated by the same process that will be used in production.

A second major contributor to the time to market is the time required to develop tooling, such as molds and dies. For some types of tooling, such as injection molding dies, the turnaround time for the design and fabrication of a tool routinely extends to several months. The long lead times are due to the fact that tooling is generally one of a kind and can be extremely complex, requiring a great deal of human attention to detail.

In present practice, tooling is a gating item not only in lead time, but in manufacturing cost as well. In fact, tooling costs often determine the minimum economic batch size for a given process.

The three issues of prototyping requirements, tooling lead time, and tooling cost are related in that it is the combination of long lead times and high cost which make it impractical to fabricate preproduction prototypes by the same process that will be used in production.

As an example of the difficulties with today's technologies, consider the use of lost wax casting to produce a batch of 100 parts of a high temperature alloy in a geometry not suitable for machining. The first step is the fabrication of an aluminum die to make the wax positives. In a typical part, the tooling cost dominates the manufacturing cost, accounting for 90 percent of the total part cost. In addition, it would commonly take 4-10 weeks to procure the aluminum tool for the wax positives.

Current options do not provide a satisfactory solution to the demands for rapid and flexible manufacturing. The goal of the current work is to develop a new manufacturing process which can produce complex three-dimensional parts directly from a computer model of the part, with no part specific tooling required. The process, called Three-Dimensional Printing, will be used to produce both functional parts and tooling for prototypes and small batch production.

1.2 Three Dimensional Printing—The Current Work. Three Dimensional Printing is a manufacturing process for the production of complex three-dimensional parts directly from a computer model of the part, with no tooling

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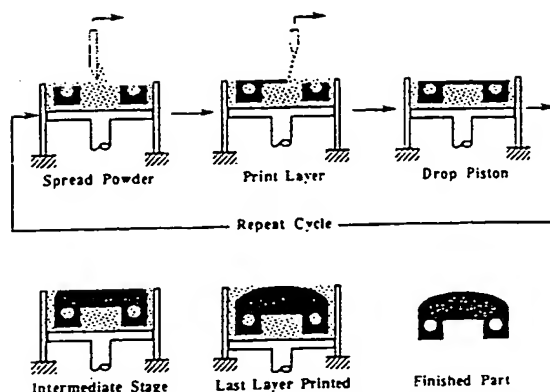


Fig. 1 Sequence of operations in the Three-Dimensional Printing process

required. Three Dimensional Printing creates parts by a layered printing process. The information for each layer is obtained by applying a slicing algorithm to the computer model of the part. An individual two-dimensional layer is created by adding a layer of powder to the top of a piston and cylinder containing a powder bed and the part being fabricated. The new powder layer is selectively joined where the part is to be formed by "ink-jet" printing of a binder material. The piston, powder bed and part are lowered and a new layer of powder is spread out and selectively joined. The layering process is repeated until the part is completely printed. Following a heat treatment, the unbound powder is removed, leaving the fabricated part. The sequence of operations is depicted in Fig. 1.

Three Dimensional Printing can be used to fabricate parts in a wide variety of materials, including ceramic, metal, metal-ceramic composite and polymeric materials. The objective of our work is to produce parts that will be used directly as prototype parts (both functional and aesthetic), and to produce parts that will be used directly as tooling.

An envisioned implementation of Three Dimensional Printing is shown in Fig. 2. Powder is applied in thin layers either by dry dispersion methods or in a liquid vehicle. The powder and printing heads are both transported by linear motors. Both powder application and "ink-jet" printing are done as full line applications in order to print the part rapidly. The part being printed is a ceramic mold for metal casting and illustrates one of the first application areas being addressed.

1.3 Related Work. Recently there has been much interest in the direct manufacture of parts from CAD memory with no tooling required. Such processes are often referred to as Desktop Manufacturing, in analogy to desktop publishing. A variety of approaches have been taken to directly fabricate a part, but in general these processes may be grouped into three areas: (1) chemical alteration of a liquid or solid using directed light energy, (2) sintering of a powder using directed light energy, and (3) selective addition of material particles or layers to an existing surface.

The most commercially advanced system is the SLA-250 from 3D Systems, Inc. [1]. The SLA-250 operates on a principle called Stereolithography wherein a focused UV laser is vector-scanned over the top of a bath of photopolymerizable liquid polymer. The UV laser causes the bath to polymerize where it hits, resulting in the addition of a solid layer to the top of the part being created. The part is lowered into the bath so that the last created layer is slightly below the surface of the liquid bath. An inherent limitation of the stereolithography process is that part overhangs and undercuts must be accommodated by building a support structure which is subsequently machined away. In order to minimize total process time, the part is not

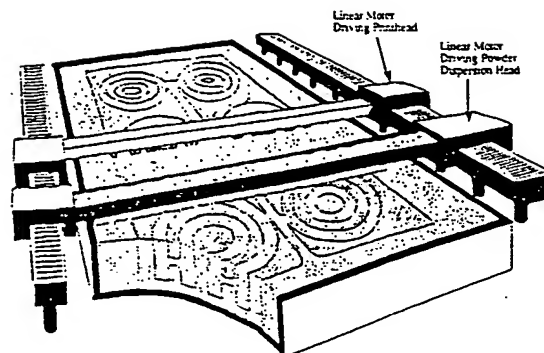


Fig. 2 An envisioned implementation of Three-Dimensional Printing. The part being printed is a ceramic mold for casting 6 identical metal parts.

completely hardened by the laser and must be post-cured in a UV "oven," resulting in some part warpage. Another current limitation is that there is a limited class of materials that may be photopolymerized. The material in present use is an acrylic based polymer which tends to be somewhat brittle.

Stereolithography is being used to create parts for aesthetic judgment and to provide checks for completeness of a CAD specification. Work is being undertaken to develop methods to use the parts as positives from which tooling is produced, for example for injection molding and metal casting [2]. At the present time, the level of attainable precision does not permit the process to be used for assembly and tolerance checking, and attainable strengths do not permit the process to be used for functional parts.

A system developed by Cubital in Israel [3] also uses a photopolymerizable liquid. However, the system includes additional process steps to avoid some of the limitations of the SLA process. The photopolymer is first wiped onto a surface and selectively exposed. A high-power mercury lamp is used instead of a laser, allowing the part interior to be fully cured during the process, and a photomask determines which portions of each layer is hardened. The noncured regions of binder are wiped off, and the layer is filled and machined flat in preparation for a new layer. Though this process bypasses some of the limitations of Stereolithography, a new problem becomes the rapid production of accurate photomasks. The masks are made by an ionographic process which has 300 "dot per inch" resolution.

The Battelle Corporation and Formigraphic Engine Company, of Columbus, OH, and Berkeley, CA, respectively, are simultaneously researching a process which uses two intersecting laser beams to chemically alter a block of material [4]. The intersecting beams can either selectively harden a "nearly-soft" block through photochemical cross-linking, or else remove portions of a solid block through photochemical degradation.

The most advanced powder sintering process, called Selective Laser Sintering (SLS), has been developed at the University of Texas at Austin [5]. Selective Laser Sintering uses a high-powered laser to sinter layers of powder. The powder is applied by a counter-rotating roller mechanism, and typical layer thicknesses are 0.004 in. Initially, plastic powders are being used, but wax, metal, and coated ceramic powders are also being investigated as candidate materials. The technology is being commercialized by DTM Corporation of Austin, TX; its first product, the SLS Model 125, employs a 20 Watt CO₂ laser and accommodates 12 inch diameter parts.

A material-additive approach is being pursued by Hydro-netics Inc. of Chicago, IL [4, 6]. Their process, called Laminated Object Manufacturing, cuts foils or sheets using a laser

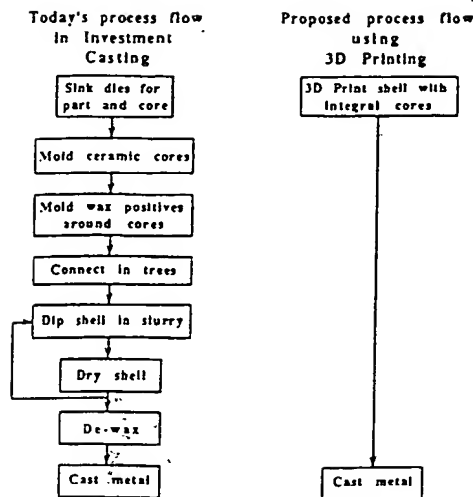


Fig. 3 The sequence of operations involved in lost-wax casting as compared to casting in molds made by 3D Printing

and stacks them to form a three-dimensional part. The layers are either glued or welded together.

Another material-additive system, called Ballistic Particle Manufacturing, uses a piezo-driven ink-jet mechanism to eject droplets of molten metal which cold-weld together. Research on this system was undertaken by Automated Dynamics Corp. of Troy, NY [7], and Perception Technologies of Easley, SC.

2 Application Areas

2.1 Overview. Potential applications for 3D Printing may be categorized in two respects: the part strength required and the dimensional control required. Some applications, such as functional ceramic parts, may require both high strength and dimensional accuracy. However, other applications may relax the requirements in one or the other category.

The initial investigation of 3D Printing has produced parts with good dimensional control, but low part strength. Accordingly, the initial applications of 3D Printing have been chosen to match these capabilities. The first two application areas are:

- The direct fabrication of ceramic cores and shells for metal casting.
- The direct fabrication of porous ceramic preforms which when infiltrated by liquid metal will form metal-ceramic composite parts.

2.2 Molds for Casting Metals. In current practice, complex, high precision castings are made by lost-wax (also called investment) casting [8]. The process begins with the fabrication of an aluminum die which is used to mold wax positives of the part to be cast. The die is usually made by electric discharge machining. Wax positives are then made by a process resembling transfer molding. If the part is to have internal voids, a second tool must be made to mold ceramic cores. The cores are inserted into the wax positives as they are molded. The wax positives with cores are then connected by hand with wax runner systems to form a tree. The tree is then dipped repeatedly into ceramic slurries with a drying cycle between each dipping operation. Following a final dry, the wax is melted and burned out of the shell mold and the mold is finally ready for casting. This sequence of operations is schematically indicated in Fig. 3. In its basic form, lost-wax casting is one of the oldest known processes.

The dies used for making the cores and the wax positives

are extremely costly and time consuming to produce. The dies must be fabricated from many parts and must have side actions in order to mold undercuts and other complex features. The dies for the wax positives can be made from aluminum, but the dies for the abrasive ceramic cores must be made of hard materials such as carbide. The cost for any die set is strongly dependent on the size and complexity of the part, but the range might span \$5,000 to \$50,000 (1992 dollars). The one of a kind nature of the dies also results in long lead times which range from 2 to 20 weeks.

The cost of dies has a tremendous impact on the cost structure for investment casting. As an example, consider a die set used to fabricate a small 1 kg steel casting with an internal cavity. Such a die set might cost \$10,000 (1992 dollars) or more, even for a simple part. Thus, if 100 parts are to be made, the amortized die cost is \$100/part. Comparing this cost to the cost of the raw steel, which would range from \$0.80 to \$5.00 depending on the alloy, we can see that tooling cost would dominate.

Three Dimensional Printing can have a significant impact on the economics of small and moderate size production runs of cast parts. By printing cores and shells directly, 3D Printing can virtually eliminate initial tooling costs, thus making prototyping and small production runs economically feasible. A critical additional benefit of 3D Printing is the reduction in lead time that will result from eliminating the need to wait for die sets to be produced.

Three Dimensional Printing can be applied to metal molding in a variety of ways. Directly printed cores can be insert molded into conventional wax patterns followed by conventional shell building and casting. Ceramic shell molds can be fabricated directly to final shape with no wax positives needed at all. In shell printing, the loose, unjoined powder washes out of the mold through the same passageways that will later admit molten metal. Such an application is schematically illustrated in Fig. 2. Finally, the greatest cost and time savings can be realized in the future by printing of integral shells and cores. The savings in processing steps is illustrated schematically in Fig. 3.

For the printing of molds, typical powder materials might include alumina, silica, zirconia, zircon, and silicon carbide. A typical inorganic binder would be colloidal silica. These materials are identical to those currently in use for the fabrication of shells and cores in the investment casting industry. When making molds with cores, it may be advantageous to print a modified binder material in the core area, which would require a second printhead.

2.3 Preforms for Metal Matrix Composites. One particularly attractive method for the manufacture of metal matrix composite parts is the "pressure infiltration" process. The process begins with the manufacture of a porous ceramic preform of the same shape as the desired final part. The preform is then infiltrated by liquid metal under the action of a pressure gradient to form the composite part. Pressure infiltration offers the key advantage over other fabrication techniques of allowing good control over the uniformity and placement of the ceramic particles.

For many applications, metal matrix composites often offer superior cost and performance as compared to materials in current use. However, the difficulty of fabricating prototypes and small production runs often results in the dismissal of composites in spite of their favorable performance.

A typical example is in the area of packages for electronic devices. Electronic packaging materials are required to provide electrical grounding, to allow thermal dissipation, to minimize the thermal stresses due to differential coefficients of thermal expansion, and to be lightweight (especially for avionic applications). Kovar, the traditional material of choice, is far from ideal because its thermal conductivity is low, its density

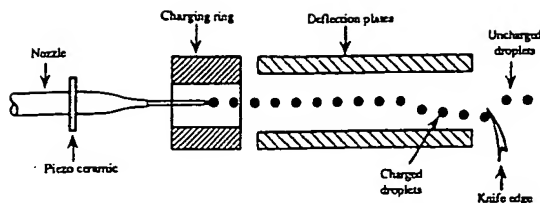


Fig. 4 A schematic of a continuous-jet printing system

is high, and its processing costs are high. Metal matrix composites offer tremendous potential for this application. Aluminum/silicon carbide composites can be tailored to have a nearly ideal match of coefficient of thermal expansion to GaAs and Alumina substrates while having a higher thermal conductivity, lower density, and lower materials cost than Kovar.

Three Dimensional Printing can be used to reduce preforms for metal matrix composites. Using 3D Printing to fabricate preforms, prototypes, and small to moderate size production runs can be made with application-specific geometry and material properties, such as particle density and coefficient of thermal expansion. This flexibility should allow for metal matrix composites to displace traditional materials and penetrate new markets such as electronic packaging.

3 Technical Options

3.1 Powder Distribution. Various methods of powder deposition may be applicable to 3D Printing. Two general areas are thought to be useful but as yet are not thoroughly tested. Particles can be applied in the dry state as is done in the selective laser sintering method for polymer particle deposition [5]. Many possible deposition mechanisms are possible for dry powders but most require that the powder flow easily when only a small amount of shear is applied. This kind of flow behavior is characteristic of granulated powders or where the particle size is greater than approximately 50 microns. The flow of finer particles is dominated by interparticle forces which produce aggregates of particles and prevent their free motion. Very fine particles may require the presence of a liquid vehicle. Chemical additives are used to augment the interparticle forces to insure that they are repulsive. These dispersants are common in paints and ceramic tape casting formulations [9].

3.2 "Ink-Jet" Binder Printing. Ink-jet printing spans a wide range of technology, which may be grouped in two categories: drop-on-demand and continuous-drop methods [10]. In drop-on-demand systems, electrical signals are used to control the ejection of an individual droplet. In continuous-drop systems, ink emerges continuously from a nozzle under pressure. The jet then breaks up into a train of droplets whose direction is controlled by electrical signals. Figure 4 shows an example of a continuous-jet system.

Drop-on-demand systems are generally of two types, piezo-driven [11] and evaporative-bubble driven. In piezo systems, a small piezoelectric element induces a pressure wave in the ink. In evaporative-bubble systems, a small resistive heater is pulsed, causing some of the ink to evaporate and form a bubble [12]. In both cases, the pressure pulse created causes a small drop of ink to be ejected from the nozzle, followed by capillary-driven refilling of the cavity.

In continuous-jet technology, the driving force for the formation of droplets is the reduction in surface energy that results from the transition from a cylindrical stream to an equal volume of spherical droplets. The breakup of the stream will take place spontaneously at a characteristic frequency, first estimated by Rayleigh [13]. The droplet formation can be regularized by the addition of piezo induced vibration of the nozzle tip. Following formation, the droplets can be charged if the liquid is slightly conductive. The charged droplets can then be

electrostatically deflected. Most commonly, binary control is utilized wherein charged droplets are deflected into a catcher and uncharged droplets are allowed to pass undeflected to the target.

Both drop-on-demand and continuous-jet systems can be operated with droplets ranging in size from 15 to several hundred microns. Drop on demand systems are limited to droplet rates of approximately 10 kilohertz due to the fact that the cavity must refill by capillary action [14]. By comparison, the Rayleigh instability used to create droplets in continuous-jet systems allows for the formation of droplets at rates of up to 1 megahertz. Both technologies are used commercially. Drop-on demand systems are used for small scale printers used as peripherals to personal computers, such as those manufactured by Hewlett-Packard [12]. Continuous-jet technology is used for very high resolution printing of color graphics in products such as the Model 3024 four color printer from IRIS Graphics of Bedford, MA. Continuous-jet technology is also to be used in high speed printing applications. An example of a high speed application is the "Dijit" printer from Diconix, Inc. of Dayton, OH, which uses a line-printing bar containing 1500 continuous-jet elements to print at speeds of up to 5 meters per second.

3.3 Binder Composition. A key element of 3D Printing will be the development of suitable binders so that regions demarcated by the printing head can be removed from the loose powder after drying or curing. There are several basic requirements that the binder system must satisfy.

- The binder solution must have a high binder content while still having a low viscosity so that it is capable of being deposited by the print head.
- A minimum conductivity may be required for continuous jet printing heads.
- The binder must dry or cure rapidly so that the next layer of particles can be applied.

Inorganic binders are useful in cases where the binder is to be incorporated into the final component. Nearly all binders are typically based on silicate systems. Silicate binders are formed from the polymerization of silicic acid or its salts in aqueous solution. The resulting solution is called a sol and can contain up to 50 wt percent inorganic material with viscosities under 10 centipoise. Sols of alumina and zirconia are also available and are used to prepare components that must withstand higher temperature [15].

Curing of the binder can involve several methods. Removal of the binder solvent by evaporation is often used but can lead to deposition of the binder at the surface of the component due to capillary-driven segregation during drying. The curing of sol-based binders is accomplished by thermal or chemical means to cause gelation of the binder and prevent segregation. Chemical additives present in the binder solution are made to thermally decompose and change its pH to a range where the sol is no longer stable. A third method is to use a gaseous reactant such as ammonia to react with the binder and form a gel.

4 Results

4.1 Summary. Both drop-on demand and continuous-jet printing of binders have been explored experimentally. The faster continuous-jet principle was used to make sample three-dimensional parts. One such part, described later, is composed of aluminum oxide powder distributed in dry form, and the binder used was colloidal silica.

4.2 Drop-on-demand Experiment. In order to assess the feasibility of joining powder using ink-jet printed binder materials, a commercial drop-on-demand ink-jet cartridge was adapted to print binder. The Hewlett-Packard "Deskjet" car-

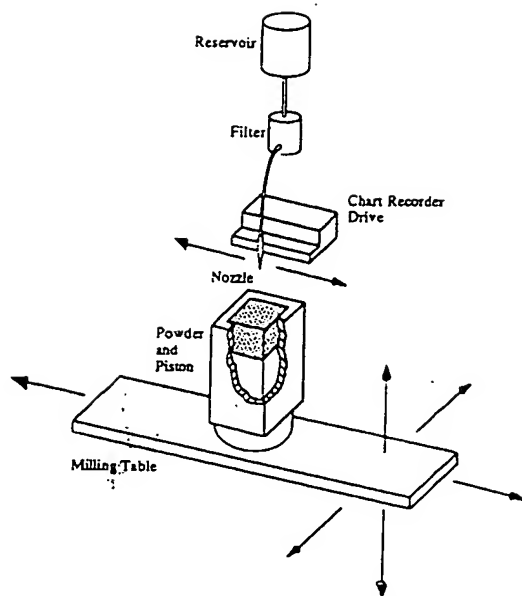


Fig. 5 Schematic of 3D Printing machine

tridge (part number 51608A) employs evaporative-bubble technology, and can print 0.002 in. diameter droplets up to 3000 times per second.

The cartridge was filled with a "spin-on glass" material from Allied Chemical (product name Accuglas X-03). This binder is derived from tetra ethyl orthosilicate (TEOS), and contains 11 percent solids by weight. The fairly low solids content and low viscosity of the binder make it suitable for printing with the adapted cartridge.

The cartridge was passed in straight lines over a smooth surface of 325 grit silicon carbide powder at a 10 in./min write-speed. After firing, a fragile, two-dimensional part was formed, comprising 0.010 in. diameter lines which were connected to form a rectangular grid.

4.3 Continuous-jet Experiment. The continuous-jet printing system illustrated in Fig. 5 was developed to demonstrate the feasibility of continuous-jet printing in this application. The printhead consists of a glass nozzle fabricated from a borosilicate pipette of 0.8 mm internal diameter. The pipette is first heated with a gas flame and elongated to form a taper. With the aid of a microscope, the pipette may then be cut along its tapered portion to create a small opening. Nozzles with an inner diameter of 10 microns and above may be formed this way.

A pressurized reservoir delivers binder at up to 150 PSI to the printhead through a 5 micron in-line capsule filter. The printhead is mounted to the "pen" holder of a modified chart recorder (Omega model 141). This chart recorder, connected to an adjustable voltage ramping circuit, can move the nozzle along one axis at a desired velocity of up to 0.6 meters per second.

The distribution of powder in fine layers is accomplished using a device that resembles a square piston (Fig. 5). The piston is driven by a stepper motor which allows vertical motion in increments as small as 0.0003 in. To create the first layer of powder, the surface of the piston is positioned slightly lower than the surrounding surface. Powder can then be scraped or rolled into the piston using a tool which rides along the perimeter of the device. For each subsequent layer, the piston is positioned slightly lower, allowing another thin layer of powder to be distributed over previous layers.

The powder piston is mounted to a motorized turntable

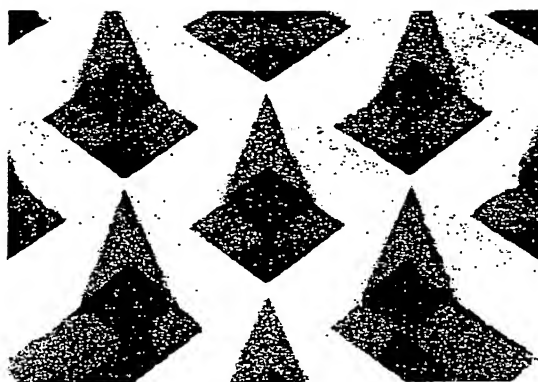
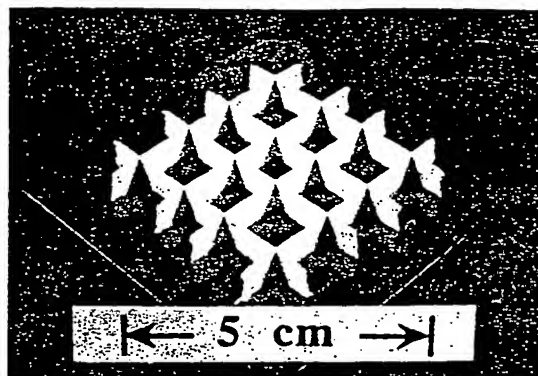


Fig. 6 Three-Dimensional part produced using the apparatus of Fig. 5, plain view (top) and magnified (bottom). Line width is 0.017 in., and height is 0.25 in.

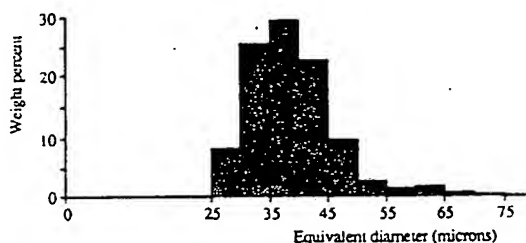


Fig. 7 Particle size distribution of alumina powder used in part

which is mounted to the slides of a milling machine; hence both rotation and x-y translation of the tray relative to the printhead mechanism is possible. Straight lines of binder are printed into the powder using the modified chart recorder mechanism. Currently, the electrostatic deflector plates normally found in continuous-jet printing systems have not been implemented. Line lengths are fixed at about 2 in. by masking off portions of the tray. The powder tray is translated or rotated to obtain a pattern of such lines. When identical patterns are printed on successive layers of powder, a three-dimensional part of finite thickness is formed. After firing, the powder tray may be emptied of powder and the part removed.

Figure 6 shows an example part made with the continuous-jet apparatus. The part was formed by printing identical grid patterns into fifty layers of powder. The materials used to make this part are suitable for the fabrication of investment casting molds. The powder is 320 grit aluminum oxide powder from Norton Co. (Worcester, MA, product number 7307). It contains a distribution of particle sizes shown in Fig. 7. The binder is colloidal silica from Nyacol, Inc. (Ahsland, MA). It

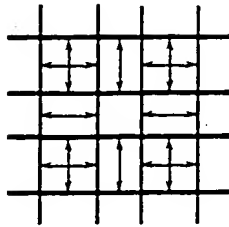


Fig. 8 Location of line spacing measurements

contains silica suspended in water in a 30 weight-percent ratio (16 percent by volume), with an average particle size of 8 nanometers. The viscosity of the binder is 8 centipoise.

The part is 0.25 in. high, fabricated in fifty 0.005 in. layers using a 0.002 in. ID nozzle. A binder pressure of 40 PSI resulted in a flow rate of 1.7 cm³/min and stream velocity of 14 m/s. The printhead write speed was 0.6 m/s, and the distance between the nozzle tip and the surface of the powder was about 1.5 cm. Firing occurred for one hour at 800°C.

To determine the accuracy of the current process, the distance between gridlines was measured optically, using a toolmaker's microscope, at the twelve locations shown in Fig. 8. The intended spacing at these locations was 0.5000 in. The twelve measurements made on the part in the green state (before firing) averaged 0.4997 in. and had a standard deviation of 0.0007 in. From a separate test of the microscope, it is estimated that the standard deviation associated with the measuring process alone is 0.0005 in. If this measurement error is assumed independent of the actual error in part dimensions, then the actual standard deviation of the part dimensions may be estimated as 0.0005 in.

After the part was fired, measurements made in the same locations averaged 0.5012 in. and had a standard deviation of 0.0019 in. When measurement error is again taken into account, then the estimated standard deviation of these dimensions becomes 0.0018 in.

The width of the gridlines, also measured at twelve locations, averaged 0.0170 in. before firing and 0.0172 in. after firing. Taking into account the measurement error, the standard deviation associated with line width was 0.0010 in. before firing and 0.0016 in. after firing.

While the accuracies obtained were quite good, there were several factors present in our experiment which could have contributed to the variability of the final part. First, the positioning of the lines was performed manually and was subject to the error of the positioning device (the milling machine). Second, any imprecision in the chart recorder mechanism itself may have introduced error during the writing of each line. Finally, the firing of the part was performed while it was adhered to a stainless steel plate, and the difference in thermal expansion between the plate and the part may have caused the part to distort slightly. None of these factors are inherent in the 3D Printing process itself; however, it is difficult to estimate their magnitude and thus account for their effect in the measurements.

5 Process Limits and Research Directions

5.1 Rate Limits. Three-Dimensional Printing has four steps which can limit the rate of the process: the application of powder layers, the printing of the binder, the infiltration of the binder into the powder, and the drying of the binder. The rate of the overall process will depend on the particular combination of technologies used for these three steps.

If dry powder dispersion is utilized, the powder application step is likely to be quite rapid, with application times of the order of 0.1–1.0 second layer. If powder dispersion in a liquid

vehicle is used, the layer must partially or fully dry prior to printing of the binder material. The drying time will depend on the specifics of the powder, binder, and solvent used, but drying times on the order of 0.1–10.0 seconds can be expected.

The rate limit associated with the printing phase can be estimated under the assumption that continuous-jet printing technology is used. The rate limit can be found by recognizing that a droplet of binder combines with a number of powder particles to form a portion of the final printed part. The element of part thus formed has a volume that is approximately twice that of the printed droplet. This follows from the fact that the droplet occupies the void space between the powder particles which is typically about 50 percent of the total volume. If we consider layers that are 100 microns thick, the volume of a layer that is .5 × .5 meters in area would be 25 cm³. Printing this layer would require depositing 12.5 cm³ of binder. Utilizing continuous-jet technology, we might use a line array with a thousand nozzles, each of which is emitting a stream of droplets with a flowrate from each stream of about 1.0 cm³ per minute. Such a print bar would require approximately 0.75 seconds to deliver the binder required to print the entire 100 micron thick layer over an area of .5 m × .5 m. Utilizing drop-on-demand printing would increase the time needed by approximately a factor of 10, as the droplet generation rate for drop-on-demand printing is lower than that for continuous-jet printing.

Infiltration of the binder into the powder is influenced by the binder's physical parameters and the velocity at which it enters a particle bed can be approximated by the Washburn equation [16]. The velocity, v , at which a liquid enters a cylindrical pore with radius, r , is:

$$v = \frac{r\gamma \cos \theta}{4\mu h}$$

where γ and μ are the surface tension and viscosity of the binder, respectively, θ is the contact angle that the fluid makes with the sides of the pore, and h is the depth the liquid has penetrated. The Washburn equation must be corrected to account for the granular nature of the particle bed, but the correction is significant only for large penetration depths and will be neglected for the purposes of discussion. It does however show that poorly wetting fluids or those with high viscosity would be slow to enter the particle bed.

A preliminary investigation of binder penetration involved two binders and three powders. A colloidal silica product from Aremco, Co. (Ossining, NY) was compared to the binder from Nyacol Co. described earlier. The Aremco binder contains a greater solids content of 50 weight percent, compared to the 30 weight percent content of the Nyacol binder. The viscosity of the Aremco binder is 35 centipoise as compared with 8 centipoise for the Nyacol material. In addition to the alumina powder used in the above described experiment, tests were performed using 320 grit silicon carbide (also from Norton Co., Worcester, MA), and alumina/silica microspheres (type SF-12 from Philadelphia Quartz, Chattanooga, TN). The silicon carbide powder is composed primarily of particles in the 30 micron range, while the microspheres contain particles between 10 and 125 microns with an average size of 65 microns.

Contact angle measurements were performed on the two colloidal silica binders. The solid surface used was a high purity alumina substrate with a density greater than 99 percent of theoretical. The surface was cleaned with chromic acid. An optical reflection technique described by Fort and Patterson [17] was used to accurately determine the angle that a single drop of binder makes with the substrate. The Nyacol contact angle was between 11 deg and 15 deg on the alumina substrate while that for the Aremco was only slightly larger, at 21 deg. These contact angles are sufficiently low to indicate that both binders will spontaneously enter alumina particle beds.

The penetration rate of each binder into particle bed was

measured by recording the time required for a 0.05 ml drop to enter a loosely packed bed of ceramic powder. A drop from a micropipette was deposited on the surface of the powder and was considered to have entered the bed when a liquid meniscus could no longer be observed. The penetration time for the Aremco binder was found to be 13 to 18 times longer than that for the Nyacol binder in each of the powders. The difference is in the same direction as that predicted by the Washburn equation, given the viscosities and wetting angles of the materials; however, the difference is somewhat larger than predicted. Qualitative agreement with the Washburn equation is also obtained by comparing the penetration times for a given binder in association with different powder beds. The penetration time for a given binder is observed to be the smallest for the ceramic microspheres. Presumably, this is the result of the large particle size and therefore larger pore size in this powder bed.

3D Printing requires that the binder change from a state that it can be ejected from the printhead to one where it bonds the particles together after deposition. Solvent-based binders would have to dry or partially dry while gel-based binders would undergo reaction to form the gel network. It is not yet clear whether optimum performance requires that the state change should occur before deposition of another particle layer. In the worst case, the binder would have to set within one cycle time for particle deposition. Thus, either drying or chemical reaction would have to occur to the point that the particle arrangement remains unaffected by subsequent particle deposition. Gelation rates of silica sols can be varied over many orders of magnitude by addition of a variety of chemical agents [18]. The fastest gelation rates reported are the order of one second or less and are usually obtained by directly mixing silica sol and the acid. Gelatin rates can be faster for other oxide sols or alkoxide solutions but a reasonable estimate of binder setting times is between 0.1 and 1 second.

Upon examination of the total process, we can see that if continuous-jet printing is used, it should be possible to build parts over a .5 m × .5 m in layers that are 100 microns thick at a rate of approximately 2 seconds per layer. This corresponds to a vertical build-up rate of 0.18 m/hour.

5.2 Geometric Control. There are two distinct issues in the control of geometry in 3D Printing: the minimum possible feature size and the variability of part dimensions. Both issues will depend strongly on the interaction of droplets of the binder with the powder. The factors controlling the interaction of powder and binder include: powder material, powder surface treatment, powder size and size distribution, powder shape, powder packing density, binder material, binder viscosity, binder surface tension, droplet size, droplet velocity, droplet frequency, temperature of powder and binder, ambient atmosphere between layer treatment, and post process treatment/heat treatment.

The minimum possible feature size will depend in part on the size of powder and the size of the droplets used in printing. As powders in the micron and submicron range may be applied, the limit on resolution will stem from the droplet size. The experience of others in the field, including experience with commercial products, indicates that printing of 15 micron diameter droplets will certainly be feasible. It is possible that smaller jets will be practical, with the lower limit to droplet size stemming from surface energy considerations in the creation of new surface area and the increased likelihood of the clogging of small jets. Another possible limit to the minimum feature size is the spreading of droplets within the powder material. As mentioned earlier, the binder penetration rate depends on the viscosity of the binder, the surface energies and wetting angle associated with the binder/powder interface, and the distribution of pore sizes in the powder bed. Thus, the distance over which fluid can migrate depends on powder

and binder properties, powder packing, and the cure rate of the binder.

In the preliminary work reported above, the minimum feature size of 0.017 in. was due primarily to spread of the droplets as the jet diameter used was 0.002 in.

Variability of part dimensions will be determined by four factors: local and cumulative accuracy of deposited layer thickness, the accuracy of drop placement, the reproducibility of the spread of the printed droplets, and the reproducibility of the dimensional changes that accompany binder cure and post processing. The shrinkage that occurs during binder curing is a strong function of particle rearrangement and will most affect low density greenbodies. At this time, little quantitative data is available; however, the preliminary results reported above indicate the potential for good dimensional control.

6 Conclusion

Three Dimensional Printing, a novel method for the fabrication of complex three-dimensional parts directly from a computer model, is under development. Three Dimensional Printing functions by the deposition of powdered material in layers and the selective binding of the powder by "ink-jet" printing of a binder material. Following the sequential application of layers, the unbound powder is removed, resulting in a complex three-dimensional part.

Both drop-on-demand and continuous-jet printing methods have been explored as methods of printing binder. Continuous-jet technology is preferred due to the higher rates possible. A continuous-jet apparatus has produced a three-dimensional ceramic part in the form of a grid which is 0.25 in. high. The ceramic powder used was alumina, and the binder used was colloidal silica. Features intended to be 0.5000 in. apart averaged 0.4997 in. apart in the green state and 0.5012 in. apart in the fired state, with standard deviations of 0.0005 in. and 0.0018 in., respectively. The minimum feature size was 0.017 in.

The initial applications of 3D printing are the direct fabrication of cores and shells for metal casting, and the fabrication of porous ceramic preforms for metal-ceramic composite parts. Research supporting these applications will investigate the factors controlling the interaction of powder and binder and their effect on production rate, control of geometry, and part strength. Equipment design issues will include the distribution of powder and the ink-jet printing of binder.

The availability of Three Dimensional Printing and other processes that transform a computer model of a part into a useful 3D part with good tolerances and surface finishes has the potential to impact manufacturing in much the same way that desktop publishing has impacted the production of documents. The result will be the ability to tailor designs to specific tasks, to shorten the cycle from design to manufacturing and to manufacture in lot sizes of one.

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References

- 1 Wohlers, T., 1989, "Creating Parts by Layers," *Cadence*, April, pp. 73-76.
- 2 Weiss, I., Levent-Gursoz, E., Prinz, F. B., Mahalingham, S., Fussel, P., and Patrick, E. P., 1990, "A Rapid Tool Manufacturing System based on Stereolithography and Thermal Spraying," *ASME Manufacturing Review*, Mar.

- 3 Pomerantz, I., 1989, "Automated Modeling Machines," *National Computer Graphics Association '89 Conference Proceedings*, Vol. 1, April, pp. 313-325.
- 4 Fallon, M., 1989, "Desktop Manufacturing Takes You From Art to Part," *Plastics Technology*, Feb., pp. 78-82.
- 5 Deckard, C., and Beaman, J., 1987, "Recent Advances in Selective Laser Sintering," *Fourteenth Conference on Production Research and Technology*, University of Michigan, Oct., pp. 447-452.
- 6 Belforte, D., 1989, "Laser Modeling Reduces Engineering Time," *Laser Focus World*, June, pp. 103-108.
- 7 Hauber, D., 1988, "Automatic Production of P/M Parts Directly from a Computer Aided Design Model," *International Journal of Powder Metallurgy*, Vol. 24, No. 4, pp. 337-342.
- 8 Kalpakjian, S., 1984, *Manufacturing Processes for Engineering Materials*, Addison-Wesley Publishing Company, Reading, MA.

- 9 Patton, T. C., 1979, *Paint Flow and Pigment Technology*, 2nd ed., J. Wiley and Sons, NY.
- 10 Heinzl, J., and Hertz, C. H., "Ink-Jet Printing," *Advances in Electronics and Electron Physics*, Vol. 65, p. 91.
- 11 Kyser, E. L., 1981, "Drive Pulse Optimization," *Advances in Non-Impact Printing Technologies*, J. Gaynor, ed., pp. 1175-1189.
- 12 Hewlett-Packard Journal, Oct. 1988, p. 56.
- 13 Rayleigh, F. R. S., "On the Instability of Jets," *Proc. London Math. Soc.*, Vol. 10, No. 4, pp. 4-13.
- 14 Arndt, P., 1974, Pulsed Droplet Ejecting System, US Patent #3,683,212.
- 15 Horton, R., 1988, "Investment Casting," *Metals Handbook*, 9th ed., Vol. 15, ASM, Metals Park, OH.
- 16 Washburn, E. W., 1921, *Physics Review*, Ser. 2, Vol. 17, p. 273.
- 17 Fort and Patterson, 1963, *J. Colloid Sci.*, Vol. 18, pp. 217-22.
- 18 Iler, R. K., 1979, *The Chemistry of Silica*, J. Wiley and Sons, NY.